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On the Jahn-Teller Effect of Mn^{2+} in Zinc-Blende ZnS Crystal

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Abstract

The excited states of Mn^{2+} in zinc-blende ZnS crystal have been studied by the Intermediate Neglect of Differential Overlap model parametrized for spectroscopy (INDO/S) within the Restricted Open-Shell Hatree-Fock (ROHF)-Configuration Interaction (CI) approximation. The effect of the Jahn-Teller (JT) active e-mode on the first excited state (a^4T_1) has been examined with respect to energy barriers and geometric distortions. The dynamical JT effect has been studied and the excited state absorption (ESA) profiles for different e-mode conformations have been calculated. Good reproduction of the experimental ESA spectrum has been obtained for nuclear arrangements corresponding to small S-Mn-S angle distortions. The off-center τ_2-mode vibrations were found to promote the JT coupling by reducing the barriers between the stable structures.

I. INTRODUCTION

The excited states of Mn^{2+} ion in cubic ZnS have been extensively studied both theoretically and experimentally.[1-5] Special attention has been paid to the Jahn-Teller (JT) effect that takes place in the low-energy degenerate quartet excited states, and especially the lowest excited a^4T_1 state that heavily influences the absorption and emission properties of ZnS:Mn.[6-8] The transitions from and to the ground state, $^6A_1 \leftrightarrow a^4T_1$, are spin and symmetry forbidden within T_d, so that coupling with asymmetric vibrational modes is believed to be the principal source of the intensity of the bands experimentally observed. Additionally, the long-lived a^4T_1 state provides the opportunity to perform excited state absorption (ESA) experiments, a technique that has proved successful in ZnS:Mn spectroscopy.[9,10] Several peaks have been observed in the visible region, the most intensive at 1.49 and 1.90 eV, but their origin has not yet been clarified. Typically, such an assignment would require a knowledge of the reference excited state geometry, a question that poses another: what is the extent of the JT distortion which results from coupling with the JT active e-modes and reduces the initial tetrahedral geometry into D_{2d} ?

In previous papers[11,12] semiempirical methods have been used to elucidate problems relating to the JT effect of Mn^{2+} in Group II-VI compounds. In this work we apply the Intermediate Neglect of Differential Overlap model parametrized for spectroscopy (INDO/S) within the Restricted Open-Shell Hartree-Fock (ROHF) approximation to the excited states of Mn^{2+} in ZnS, and follow these calculations with a Configuration Interaction (CI) treatment. The aim of this study is *(i)* to see how well this model reproduces the

1

spectroscopic features of the above system, *(ii)* to reexamine the JT effect taking place for the first excited state of ZnS:Mn, and *(iii)* to relate the calculated properties to the experimental ESA spectra. For these studies we will use the INDO model[13-16] implemented in the program ZINDO.[14-16] This model has been used successfully to study JT effects in transition-metal complexes[17] and in small clusters.[18-20]

II. METHOD AND MODEL

In this work we have adopted a model that reflects the experimental zinc-blende ZnS:Mn structure: a tetrahedral MnS_4 cluster with Mn-S bond length 2.35 Å. As shown in previous studies,[4,12] the inclusion of the surrounding lattice is necessary to correctly assess the transition energies[4] and the JT splittings.[12] Toward this end, we have considered an external potential modeled by 12 point charges, each having +0.5 charge, situated at the crystallographic positions corresponding to Zn lattice sites in ZnS - 3.82 Å away from the central Mn^{2+} ion. The addition of 12 point charges creates a neutral cluster of overall T_d symmetry and forms an external potential that simulates the rest of the lattice. As shown below, this model reproduces well the absorption spectroscopy of the ground state, when the Franck-Condon principle is active. The excited state spectrum, however, is from a JT distorted structure in which the lattice charges have been hold fixed in their ground state positions. There is no easy way to allow geometric relaxation of the lattice within this model. We believe that the latter effect is small as (1) the neighbors of the cluster represented by point charges are bound to three other lattice atoms

2

helping to anchor their positions, and (2) the JT distortions, themselves, are presumably small. We recognize, however, that our calculated distortions under this model might be underestimated. Although the calculated energy of the JT distorted cluster might be too high in the absence of lattice relaxation, it is difficult to translate this error into errors of transition energies from the distorted first excited state to the other higher lying states. An estimate of 0.08-0.10 eV for the lattice relaxation of the first excited state can be made assuming a model suggested earlier[12] that considers second neighbor correlated motion. These values are obtained for small second neighbor displacements , typically 0.005 Å, and angle distortions up to $\pm 20°$ produced by the JT active e- mode.[12] Some of the higher excited states that are reached from the first excited state (ESA) might be similarly distorted, and the errors cancel, others might not distort or distort along a different symmetry, leading us to underestimated transition energies. In this latter case, the maximum error might be estimated at 0.16-0.20 eV These effects are small, at least with respect to the errors introduced in this model, and in the computation.

Spectroscopic INDO parameters have been used here as originally parametrized.[14,15] Extensive configuration interaction (CI) calculations have been carried out that include all CI single (CIS) excitations. At this level of approximation we hope to have taken into account all important contributions coming from d-d and s,p-d transitions. Since the ground state ($^6A_1$) and the quartet excited states differ in spin multiplicity, they have been calculated separately and the identification of the excited states was based on energy and transition moments and their splitting patterns upon reduced symmetry.

All states have been thoroughly checked with respect to configuration origin: $^6A_1$ $(e^2t_2^3)$; $^4T_{1,2}$ $(e^1t_2^4, e^2t_2^3, e^3t_2^2)$; ^4E, $^4A_1$, $^4A_2$ $(e^2t_2^3)$. Additionally, the transition energy to the lowest doublet state a^2T_2 has been calculated, a state stemming from 10 possible $e^xt_2^{5-x}$ configurations with x ranging from 0 to 4, and all contributing slightly to the ZnS:Mn spectrum due to their double spin-flip origin. We note that two of the configuration involved in this state ($e^4t_2^1$ and t_2^5) arise from double excitations from the ground state configuration ($e^2t_2^3$) and their inclusion requires another type of CI (CI singles and doubles) so that the calculated state energy cannot be directly compared with that of the quartet excited states. This difference, however, appears to be of marginal importance as the a^2T_2 state is calculated usually much higher in energy than that of the first excited state.[4,5]

Two major types of JT normal modes have been experimentally detected:[6,7]

(i) the e-mode involving a pure bending vibration of the S-Mn-S angles and preserving the S_1-Mn-S_2/S_3-Mn-S_4 dihedral angle the same as in the original T_d structure (90°). The initial T_d symmetry of the impurity center is reduced by the e-mode to D_{2d}.

(ii) the τ_2-mode that can be modeled by off-center movement of the central metal atom towards one of the ligands. This mode is predominantly a stretching one and reduces the tetrahedral environment to C_{3v}. The τ_2-modes were found both theoretically and experimentally to be an order of magnitude less active than the normal e-mode.[7]

The above two modes do not mix through the vibronic Hamiltonian under T_d symmetry. However, their products can transform into each other at reduced symmetries: Table 1 shows the term splittings that are observed for structures symmetries lower than T_d. As seen from Table 1, the first excited $^4T_1$ state can be brought into JT minimum

either through an e-mode and a subsequent ^4E splitting to $^4B_1$ and $^4B_2$ in C_{2v}, or by an off-center Mn^{2+} movement that reduces the symmetry to C_{3v}, followed by further coupling with a normal mode that reduces the symmetry to C_{2v}. This latter vibration is a third mode under consideration in this work: the bending e-mode of the C_{3v} group that distorts the structure to C_{2v}. This mode is nearly the same as in T_d, with the only difference that it takes place at unequal Mn-S bond lengths.[21] The resulting geometries can easily be converted to D_{2d} by simply having the central atom relax back to its original position.

The JT distortions considered above may occur only if the excited state under consideration is long enough lived to provide the necessary time for the nuclear relaxations. As already mentioned, we concentrate here exclusively on the stabilization of the first excited state a^4T_1, a state which is spin and symmetry forbidden in T_d, and is therefore expected to be long lived . Higher energy states are of minor importance for this work for they are likely to internally convert or intersystem cross to either this state or ground state. The lowest excited state is observed to be populated in the ESA experiments.[9,10]

The predominantly manganese $3d$-orbitals have been carefully monitored during the mode simulations in order to avoid state mixings. Typically, the energy ordering of the d-orbitals was in accordance with the theoretical predictions for the above symmetries. Only at very large angle or bond length distortions, is a reordering of the d-orbitals observed due to the higher repulsion, but these structures are of no practical importance as they reflect extreme geometries that are not physically reachable under normal conditions.

The JT theorem proves that states of non-linear molecules that are spatially degenerate, will distort to a lower symmetry that will destroy the spatial degeneracy, i.e. there

5

is at higher symmetry always a normal mode that will reduce the symmetry. The isolated MnS_4^{6-} center in the excited a^4T_1 state would normally distort. The presence of the ZnS lattice, however, may alter the dynamics of this system somewhat and either prevent the distortion or introduce a barrier. We will see that the latter is the case for a simple point-charge model of the lattice.

III. RESULTS AND DISCUSSION

The method and model described in the previous section have been used to examine the absorption spectrum of ZnS:Mn in its ground state (T_d) geometry. The results are summarized in Table 2 where they compared with the *ab initio* calculations of Janssen and Richardson.[4]

The INDO/S calculations give qualitatively the same results as do the *ab initio* calculations; they are in somewhat better agreement with experiment. The assignment of the first 3 bands is in agreement with that generally accepted. Ambiguity exists in the literature on the relative position of the a^4E and $^4A_1$ states originating from the same configurations, some authors calculating a^4E above $^4A_1$,[4] others predicting the reverse ordering.[3,22] Our calculations yield the $^4A_1$ state 100 cm^{-1} higher in energy than the a^4E term.

The assignment of the higher lying quartet states is in line with that given elsewhere.[4,5] The fourth and fifth absorption bands, in increasing energy, are still controversial (see Ref. 4 and references therein) due to the large mixing of states in this energy region. The location of doublet states (a^2T_2) and the possible influence of this state on the observed

6

spectrum as suggested earlier[5] is in doubt. On the basis of these calculations, this state is high in energy (3.83 eV) and is expected to have very low intensity due to the spin selection rules. We suggest that it has little influence on the ZnS:Mn spectroscopy.

The electron distribution for the model MnS_4^{6-} ground state was found to be close to that of the ionic case: $3d^{5.06}(e^{2.02}t_2^{3.04})\,4s^{0.68}\,4p^{1.15}$ according to the Mulliken population analysis. Since the Mn $4s$ and $4p$ orbitals have their maxima within the ligand region, they can be considered practically depopulated[4] and the total charge on the central Mn atom estimated $+1.94$. A similar result was obtained from the *ab initio* calculation which yielded a $+2.02$ charge on the Mn atom.[4] However for these calculations the Mn-S bond distance was set equal to that in cubic MnS, 2.43 Å, as opposed to that used here, 2.35 Å. The long distances might be expected to lead to greater ionic character.

In order to estimate the JT distortions, motion along the asymmetric e-mode was examined. Both ground and first excited state energies have been calculated as a function of the bending S-Mn-S angles. Only the lowest component of the a^4T_1 state is shown in Figure 1a. Higher energy terms mix to a larger extent as the distortion progresses, and these are of minor importance for the present study as already mentioned.

The two curves shown in Figure 1a can be used to quantify the JT effect for the Mn^{2+} impurity center in the ground and excited states. A large asymmetry of the potential curve exists for the $^6A_1$ ground state due to the inequivalency of the compressed and elongated D_{2d} forms. The $^6A_1$ term has a minimum at the tetrahedral structure in agreement with experiment. The theoretical maximum lies at S-Mn-S angle equal to $180°$ corresponding to

D_{4h} symmetry. We should to note, however, that such extreme structures are improbable since the surrounding lattice would hinder them, as previously discussed elsewhere.[12] For this reason, we constrain the presentation of our results in Figure 1a to angle distortions of $\pm 40°$ although these limits might also be considered too great.

The excited a^4T_1 state shows stabilization with the T_d e-mode in accordance with previous theoretical and experimental studies.[2,4,6,7] The left part of Figure 1a corresponds to elongated D_{2d} forms (S-Mn-S angles smaller than in T_d) for which the lowest split state is the ^4E term. No stabilization has been observed in this case, as determined previously.[12] A slight minimum can be seen at the T_d geometry for which the a^4T_1 term is of lowest energy. This minimum must result from the lattice model that we are using and not allowing the cluster to distort. The JT theorem dictates a distortion from T_d symmetry. Further compression of the cluster brings the system into a new flat minimum with S-Mn-S angle of 138° (29° distortion) and then into a slightly deeper energy region that smooths around the D_{4h} structure. For the compressed D_{2d} form, the $^4A_2$ state was found to be of lower energy and its energy profile strongly supports the experimental findings on the dynamical JT behavior.[6,7] The favorable D_{2d} distortion should pass through a maximum of approximately 650 cm^{-1} (see Figure 1b) at an S-Mn-S angle of 114°, and then the potential curve flattens smoothly.

At the same time, the off-center τ_2-mode, which distorts the T_d to C_{3v}, brings about no substantial stabilization of the first excited state (see Figure 1c), the ^4E and $^4A_2$ in C_{3v} interchanging their relative positions depending on the direction of the distortion. Two shallow minima of approximately 3 cm^{-1} have been detected for very small distortions

corresponding to off-center displacements of ± 0.01 Å. This result is in agreement with the experimental and theoretical findings[6,7,11] showing that the JT splittings due to the τ_2-mode are negligibly small compared to that produced by the e-mode. As seen from Figure 1c, this mode *alone* is of marginal importance for the excited states and the electron transitions in ZnS:Mn. Combined with the C_{3v} bending e-vibration, however, it produces the same stabilization effect as that shown in Figure 1a. Such a mode combination may be possible due to the fact that both τ_2- and e-modes in T_d lead to a ^4E product that is also subject to JT distortion.

The JT barriers for the combined distortion are considerably lower than that observed for the T_d e-mode alone: the 650 cm^{-1} barrier shown in Figure 1b is reduced to 350 cm^{-1}. As mentioned before, the C_{3v} and D_{2d} forms may interconvert through C_{2v} provided there is time enough for the nuclear motion. Since the lowest a^4T_1 component for the compressed D_{2d} form (S-Mn-S angles larger than in T_d) is always the $^4A_2$ state and the latter term is symmetry forbidden for all the symmetries present, this requirement is likely fulfilled. The energy barriers thus observed are easy to overcome at ambient temperatures and facilitate the dynamical JT effect for the excited state. It must also be recalled that any relaxation of the lattice should also lower this barrier. The conclusion that can be drawn from the above considerations is that the e-mode conformations can be reached either by direct distortion or through a sequence of asymmetric modes that has sufficiently lower barriers.

We proceed further with the calculation of excited state absorption (ESA) spectra[9,10] arising from excitations from the first excited state to the higher lying states. Such a calculation is unique in the sense that it can provide direct theoretical evidence on the

9

existence, extent and type of the JT distortions taking place in the ZnS:Mn excited states.

The computational scheme we have used was the following: *(i)* calculation of the quartet excited states by INDO/S method within the ROHF self-consistent field (SCF) approximation at CIS level; *(ii)* calculation of the the oscilator strengths for the transitions from the first 3 CI states to the higher terms using the ZINDO algorithm.[15,16,23] This particular step provides the inclusion of all the a^4T_1 components at any symmetry and contributes significantly to the completeness of the ESA spectrum. *(iii)* Lorenzian band simulation around each non-zero ESA peak and subsequent convolution of the delta functions to a normalized Lorenzian function of a proper width. The latter width has been set 1000 cm^{-1}, close to the average value observed in the ZnS:Mn absorption spectra.

The calculated ESA spectra are given in Figures 2a-d. These plots represent the JT D_{2d} structures that can be obtained through distortions at different angles. The off-center τ_2-mode produces ESA spectra that cannot be related with experiment (bands too high in energy), but its *e*-mode combination that leads to a structure of C_{2v} symmetry gives ESA profiles similar to those in D_{2d}.

First we note that the ESA spectrum calculated for the T_d geometry (Figure 2a) - transitions from the a^4T_1 state to higher lying terms - shows little resemblance to the experiment. An intense band is observed at about 15,000 cm^{-1} (1.86 eV) that can be assigned to the experimental 1.9 eV band maximum, but there is a complete lack of other bands in the 1.1 - 2.3 eV region where the experimental spectrum was recorded.[9,10] This result strongly suggests that the excited state is not of $^4T_1$ type in T_d.

10

Further distortion of the tetrahedral environment around the Mn^{2+} ion in the excited state, leads to the appearance of the experimental peaks as shown in Figures 2b-d. Examining the theoretical ESA structures and intensities, we can conclude that the best reproduction of the experimental ESA spectrum is obtained at relatively low values of the S-Mn-S angle distortions, corresponding to slight D_{2d} type atom rearrangements. The best fit with the experimental ESA spectrum has been obtained at S-Mn-S angle of 115°, close to the predictions based on the excited state energies by both *ab initio*[8] and semiempirical studies.[12]

In all cases displayed in Figure 2, a group of IR bands centered at about 4000 cm^{-1} (0.5 eV) is present in the ESA spectrum. Contrary to the 1-2 eV peaks which are dominated by Mn $3d$-configurations of the type e^2(triplet)t_2^3(doublet), these particular IR bands have their origin from states e^1(doublet)t_2^4(triplet) that involve $e{\rightarrow}t_2$ electron transitions. The existence of these bands needs experimental verification.

Finally we would like to mention, once again, that the present ESA simulation should be viewed as further evidence of the presence of a strong JT effect for the ZnS:Mn excited states. The theoretical ESA spectrum is calculated by the superposition of a large set of initially T_d split terms that stem from a coupling with the JT active e-mode, and is therefore a characteristic of the whole assembly of excited states rather than the first excited state alone.

ACKNOWLEDGMENT

11

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Table 1 Term splittings for different symmetries involved in the JT distortions.

T_d	D_{2d}	C_{3v}	C_{2v}
T_1	A_2+E	A_2+E	$A_2+B_1+B_2$
T_2	B_2+E	A_1+E	$A_1+B_1+B_2$
E	A_1+B_1	E	A_1+A_2
A_1	A_1	A_1	A_1
A_2	B_1	A_2	A_2

Table 2 Calculated and experimental band energies (eV) for ZnS:Mn; *ab initio* data taken from Ref. 4.

Tansition	Ab initio	This work	Experiment
$^6A_1 \rightarrow a^4T_1$	2.68	2.72	2.34
$\rightarrow a^4T_2$	2.83	2.76	2.49
$\rightarrow a^4E$	2.96	2.78	2.67
$\rightarrow\ ^4A_1$	2.96	2.78	2.67
$\rightarrow b^4T_2$	3.31	3.18	2.89
$\rightarrow b^4T_1$	3.39	3.47	3.19
$\rightarrow b^4E$	3.52	3.56	-

Figure Captions

Figure 1   (a) Ground and first excited state energies as a function of the e-mode distortion parameter, the ground state $^6A_1$ energy at T_d-geometry taken as a reference. (b) closer view of the local minima observed for the a^4T_1 state. (c) ground and first excited state potential curves produced by the τ_2-mode.

Figure 2   Excited state absorption (ESA) spectra calculated for: (a) the initial T_d structure, and the D_{2d}-geometries resulting from the e-mode distortion by (b) 5°, (c) 10° and (d) 15° of the initially tetrahedral S-Mn-S angles. Dashed lines indicate the positions of calculated ESA peaks.
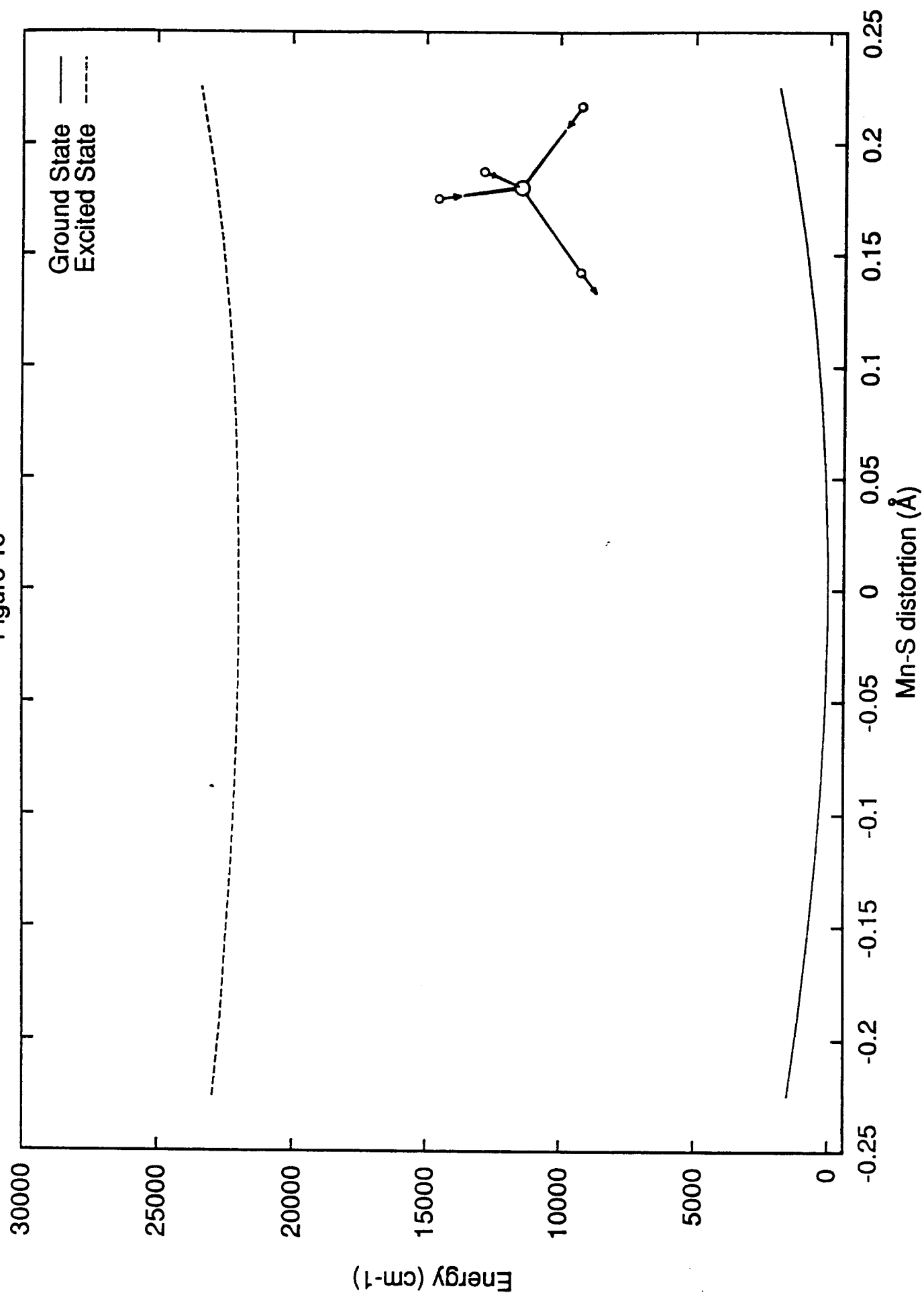
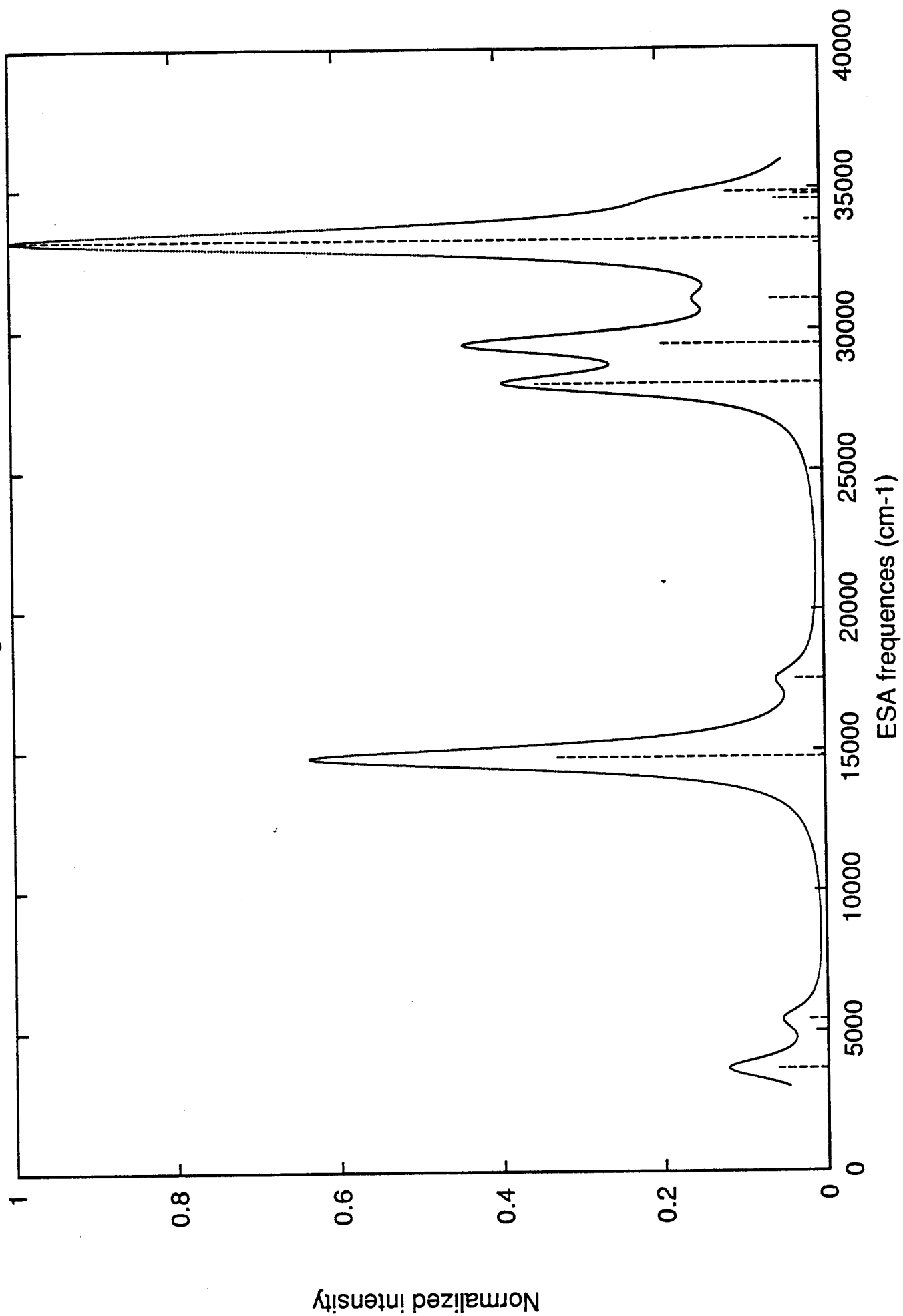Figure 1a
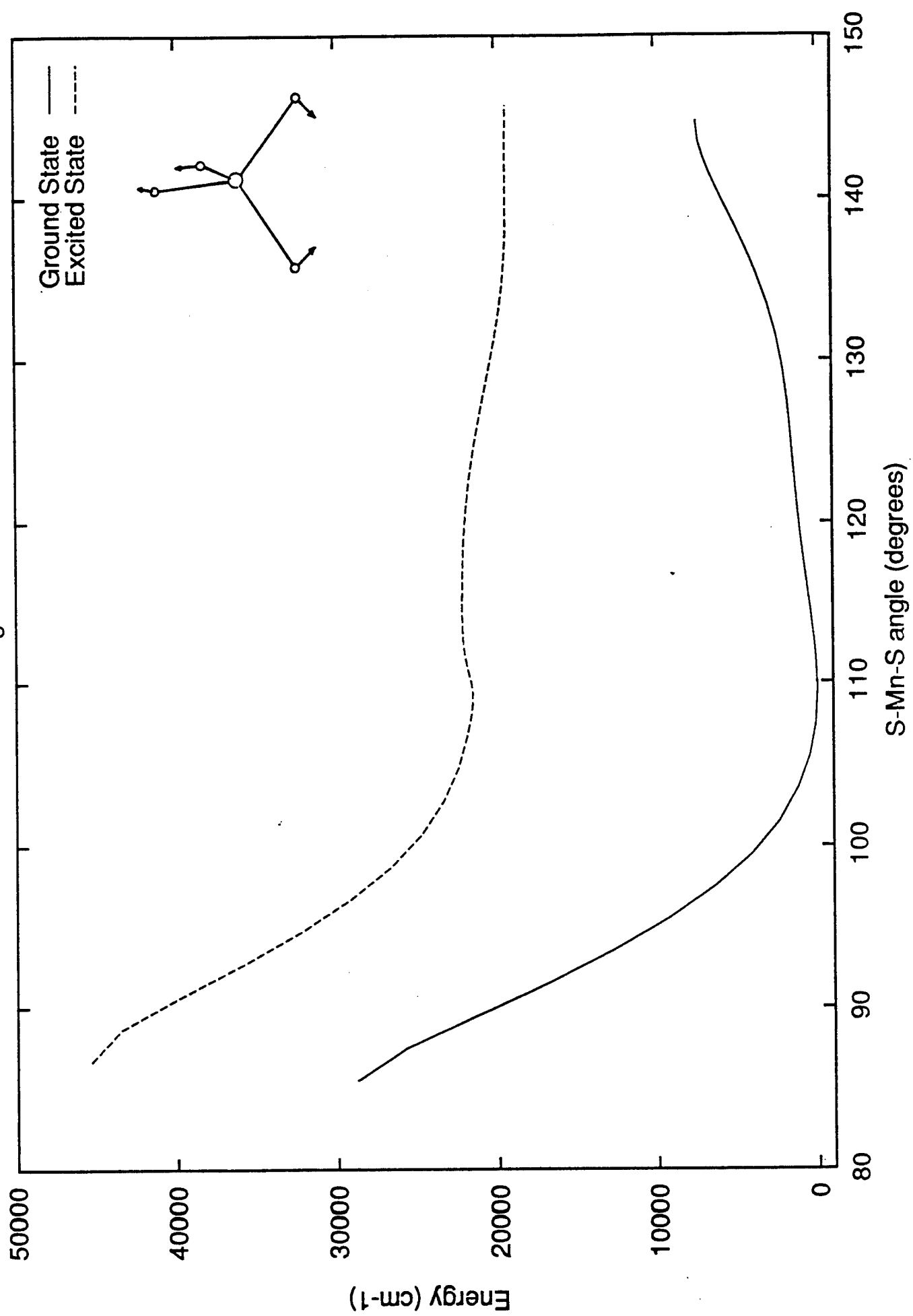
Figure 1b
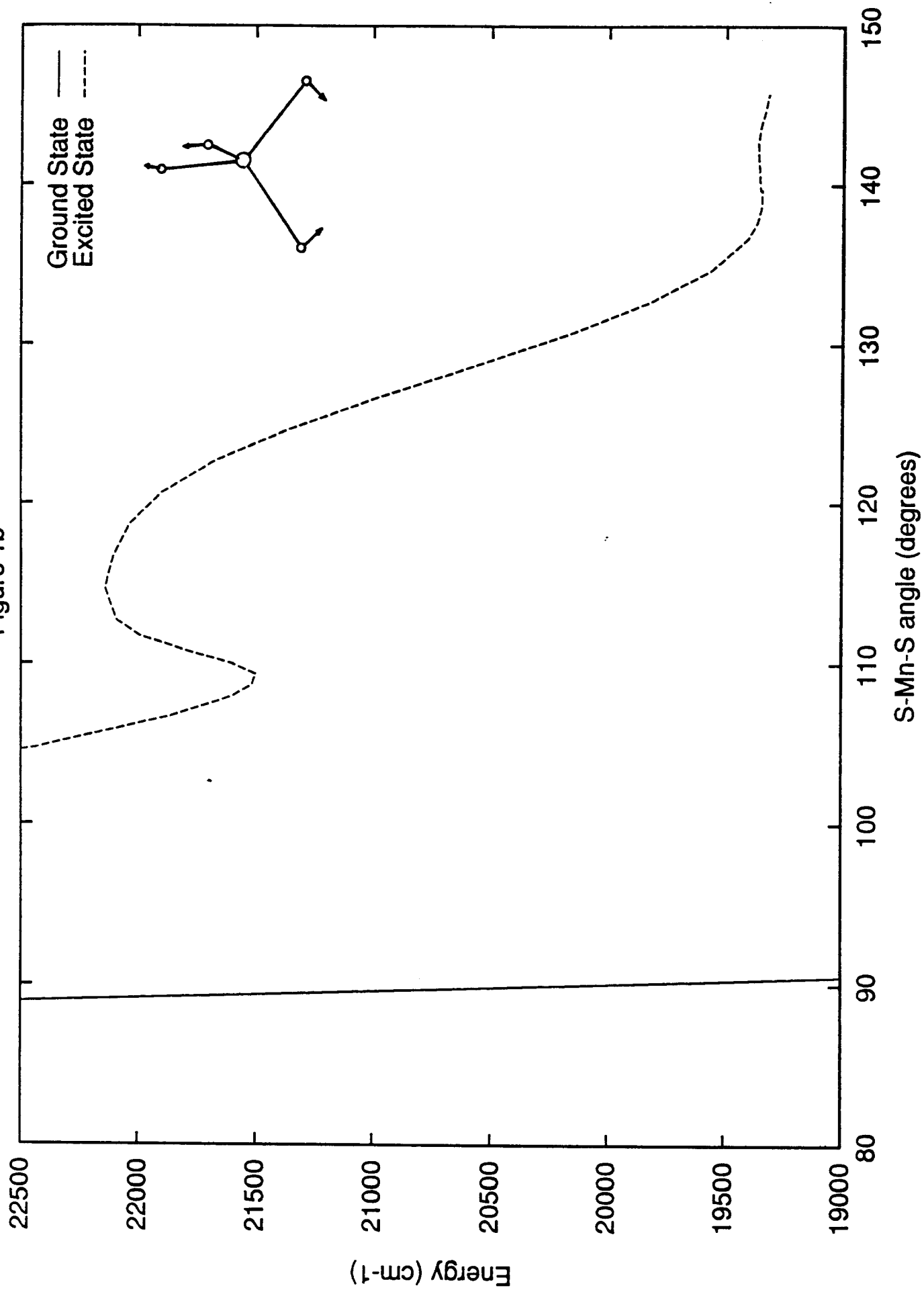
Figure 1c

Figure 2a

Figure 2b

ESA frequences (cm-1)

Normalized intensity

Figure 2c

Figure 2d